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Nucleobase appended viologens: Building blocks for new optoelectronic materials

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ABSTRACT

We describe here the fabrication, characterization and possible applications of a new type of optical material – consisting of 4,4′-bipyridinium core (“viologen”) and nucleobases i.e. adenine and/or thymine made by H-bonding. The viologen–nucleobase derivatives were used to construct supramolecular structures in a “biomimetic way” with complementary oligonucleotides (ssDNA) and peptide nucleic acids (ssPNA) as templates. The new nanostructured materials are expected to exhibit enhanced optical and optoelectronic properties with application in the field of supramolecular electronics. Such viologen derivatives could be significant in the design of new 2D and 3D materials with potentially application in optoelectronics, molecular electronics or sensoric.

1. Introduction

The molecules with multiple functionalities are promising building blocks for construction of functional materials with enhanced properties. This is because the combination of two or more distinct functions may have a cumulative effect on the overall properties and features of the corresponding material.

Particular attention has been directed toward the synthesis of compounds with two functionalities consisting in a core responsible for physico-chemical properties (i.e. electrochemical, optical, etc.) and nucleotide bases as capping groups capable of molecular recognition [1–10]. A major motivation of designing such compounds lies in the ability of nucleobases to direct the self-assembly process of functional molecules which may result in a modulation of physico-chemical properties of the corresponding materials. Optical materials obtained by highly ordered assembly of π-stacked distyrylbenzenes and oligoadenines as template were described by the group of Wong [1]. Well-defined nanofibrous structure with lengths of several hundred nanometers was self-assembled by oligoadenines (dA_{20}), and thymine-appended distyrylbenzene through binary complementary A—T hydrogen bonding and π–π stacking interaction. Numerous coordination polymers based on modified 4,4′-bipyridine, such as 4,4′-bipyridine oxide which exhibit 2D sheet and 3D motif formed by hydrogen bonding and π–π interaction have been well documented [2].

In this work we aimed to develop new optical/optoelectronic materials consist of a redox units with well-known electrochemical properties, and biologically activity. The building blocks molecules containing of redox active 4,4′-bipyridinium core so called “viologen” with are capping by two (**1**) and three (**4**) thymine units, adenine (**2**) and thymine/adenine (**3**), respectively. The combination is unusually and offer two molecular functionalities: viologen and nucleobases. The 4,4′-bipyridinium unit, known as a good electron acceptor, used in electrochemical processes and the nucleobases might act as electron donors, capable of fast electron-transfer reactions. The acceptor and the donor tails are electronically isolated trough a polymethylene spacer will lead to a separation of the molecular orbitals HOMO (located on the acceptor tail) and LUMO (located on the donor tail) which is of great interest for the field of molecular electronics. On the other hand, the nucleobase are capable of hydrogen-bonding with complementary biological target to lead to construction of new functional 2D and 3D materials. The donor–acceptor relationship between the viologen and nucleobase and the electrochemical properties with regard on the optical and redox properties was especially addressed. Depending on the molecular structure, if 4,4′-bipyridinium core is capping with a pyrimidine, a purine, or purine/pyrimidine unit, significantly different characteristics in optical and electrochemical behavior was observed. The viologen–nucleobase derivatives **1**–**4** were used to construct

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supramolecular structures in a "biomimetic way" with complementary oligonucleotides (ssDNA) and peptide nucleic acids (ssPNA) as templates. The viologen derivatives appended by nucleobases have been proved to be excellent building blocks candidates for such purpose. Such viologen derivatives could be significant in the design of new 2D and 3D materials with potentially application in optoelectronics, molecular electronics or sensor.

2. Material and methods

2.1. Materials

All chemicals were purchased from Merck (D-Hohenbrunn), Sigma–Aldrich and Fluka. Solvents were of laboratory grade. Elemental analyses: VarioMICRO cube. UV Spectra: 8453 UV–Vis Spectrophotometer (Agilent, Germany) λ_{max} in nm (ε in M^{-1} cm^{-1}). NMR Spectra: Bruker AMX-500 spectrometer; ^{1}H: 500.13 MHz, ^{13}C: 125.7 MHz; chemical shifts δ are given in ppm relative to the solvent signal peaks as internal standard for ^{1}H and ^{13}C NMR.

2.2. Electrochemistry and spectroelectrochemistry

DMF and $NaClO_4$ (puriss., electrochemical grade) were purchased from Sigma–Aldrich and Acros Organics for cyclic voltammetry and spectroelectrochemical studies. CVs were measured under Ar with the potentiostat PGSTAT 302N from AUTOLAB controlled by a PC running under GPES from Windows, version 4.9 (ECO Chemie B.V.); a glassy carbon electrode (GCE) from Metrohm (Germany) with an electrochemical active surface area of $A = 0.031$ cm^2 was used for CV. The working electrode surface was polished with Al_2O_3 before the measurement. The reference electrode was Ag/AgCl (3 M KCl in water) and the counter electrode was a Pt wire. The cell used for SEC–UV–VIS measurements of compounds **1**–**3** in solution was an H-Type spectroelectrochemical bulk electrolysis cell [13]. The reference was an Ag/AgCl electrode immersed in an electrolyte vessel filled with LiCl (2 M in ethanol), separated from the cell by a glass frit and the counter electrode was a Pt-foil. The working electrode was 0.039 g of graphitized carbon felt GFA-5 of approximately 0.021 m^2 BET area from SGL carbon, the electrochemically active area of which is not known. Absorbance changes were measured in conjunction with an Agilent 8453 Diode Array Spectrophotometer.

2.3. Temperature-absorption dependence and CD characterization

Tm experiments of the mixtures of 4,4′-bipyridinium-thymine derivatives **1**, **4**–**7** with oligonucleotides (dA_n) respectively analogue peptide nucleic acid A_{10}-PNA in phosphate buffer solution (see general preparation procedure section) were monitored with a Cary 100 UV–Vis Spectrophotometer. The measurements were consist in monitoring the absorbance at 260 nm while the sample was heated from 20 to 80 °C with 1 °C/min ramp temperature after 5 min of equilibration time. CD spectra were recorded at 20 °C with a J-600 Spectropolarimeter (Jasco, Japan).

3. Experimental

3.1. Mixture preparation of 4,4′-bipyridinium-thymine derivatives with oligonucleotides or analogue peptide nucleic acids

Corresponding volumes of aqueous stock solutions of oligonucleotide (dA_n) or peptide nucleic acid A_{10}-PNA and respectively 4,4′-bipyridinium-thymine derivative were mixed in a phosphate buffer (pH = 7) to afford an equimolar ratio of thymine/adenine. The solution volume was adjusted to a final concentration of 20 μM thymine, respectively adenine units. Resulted mixture was heated up to 80 °C for 5 min and cooled down slowly to room temperature. The mixture solutions were then stored at 4 °C prior optical characterization.

3.2. 1,1′-Bis[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)-propyl]-4-(pyridin-4-yl)pyridinium dibromide (1)

1-(3-Bromopropyl)-5-methyl-3H-pyrimidine-2,4(1H,3H)-dione (1.756 g, 7.1 mmol) and 4,4′-bipyridine (0.24 g, 1.54 mmol) were dissolved in dry DMF (60 mL) and stirred at 80 °C for 4 days. Resulted light-yellow precipitate was filtered, washed with DMF (20 mL), Et_2O (20 mL) and dry in ultra-high vacuum at 45 °C to afford **1** as bromide salt (0.76 g, 1.16 mmol, 76%). ^{1}H NMR (500 MHz, D_2O, 30 °C): δ = 9.26 (d, J = 6.62 Hz, 4H), 8.66 (d, J = 6.30 Hz, 4H), 7.60 (s, 2H), 4.93 (t, J = 7.25 Hz, 4H), 4.05 (t, J = 6.62 Hz, 4H), 2.65 (quin, J = 6.70 Hz, 4H), 1.96 ppm (s, 6H); ^{13}C NMR (125 MHz, D_2O, 30 °C): δ = 166.87(s), 152.31(s), 150.31(s), 145.76(d), 142.49(d), 127.16(d), 111.47(s), 59.43(t), 45.25(t), 29.53(t), 11.33 ppm (q); elemental analysis calcd (%) for **1** as PF_6^- salt $C_{26}H_{30}F_{12}N_6O_4P_2$ (780.48): C 40.0, H: 3.87, N 10.77; found C 39.69, H 3.60, N 10.71.

3.3. 1,1′-Bis[2-(6-amino-9H-purin-9-yl)ethyl]-4-(pyridin-4-yl)pyridinium dibromide (2)

1-[2-(6-Amino-9H-purin-9-yl)ethyl]-4-(pyridin-4-yl)pyridinium monobromide (0.382 g, 0.96 mmol) and 9-(2-bromoethyl)-9H-purin-6-amine (0.6 g, 2.48 mmol) were dissolved in distilled water (30 mL) and stirred at 80 °C for 17 days. In the 10th and 14th day after reaction start, a new quantity of 9-(2-bromoethyl)-9H-purin-6-amine was added (0.2 g, respectively 0.12 g). After 17 days, reaction mixture was cooled down to 21 °C and subsequently, acetone (80 mL) was slowly added. Resulted precipitate was separated by filtration, washed with acetone (10 mL) and dry under reduced pressure to afford the product **2** (0.523 g, 0.82 mmol, 85%). ^{1}H NMR (250 MHz, DMSO-d_6, 30 °C): δ = 9.19 (d, J = 6.91 Hz, 4H), 8.63 (d, J = 6.91 Hz, 4H), 8.11 (s, 2H), 7.78 (s, 2H), 7.26 (br. s., 4H), 5.14 (t, J = 5.30 Hz, 4H), 4.85 (t, J = 4.10 Hz, 4H); ^{13}C NMR (125 MHz, D_2O, 30 °C): δ = 155.82(s), 152.75(d), 150.69(s), 149.19(s), 146.21(d), 142.02(d), 127.34(d), 118.19(s), 61.52(t), 44.09(t); elemental analysis calcd (%) for **2** as PF_6^- salt $C_{24}H_{24}F_{12}N_{12}P_2 + 0.8\ H_2O$ (770.46 + 14.4): C 37.41, H 3.14, N 21.82; found: C 36.73, H 3.29, N 21.41.

3.4. 1-[2-(6-Amino-9H-purin-9-yl)ethyl]-1′-[3-(5-methyl-2,4-dioxo-3,4-dihydropyrimid-in-1(2H)-yl)propyl]-4-(pyridin-4-yl)pyridinium dihexafluorophosphate (3)

1-[2-(6-amino-9H-purin-9-yl)ethyl]-4-(pyridin-4-yl)pyridinium monohexafluorophosphate (0.45 g, 0.97 mmol) and 1-(3-bromopropyl)-5-methylpyrimidine-2,4(1H,3H)-dione (0.72 g, 2.19 mmol) were disolved in dry DMF (20 mL) and stirred at 80 °C for 70 h. Resulted precipitate was filtered, washed with DMF (5 mL) and acetone (20 mL). After drying in vacuo, the resulted solid was dissolved in water (20 mL) and treated with aqueous solution of NH_4PF_6 (4 ml, 10 wt%). The resulted precipitate was separated by filtration, washed with water (5 mL) and dry in vacuo to obtained product 3 as a white solid yield 281 mg (0.281 g, 0.44 mmol, 45%). ^{1}H NMR (250 MHz, CD_3CN, 30 °C): δ = 9.78 (br. s, 1H), 8.94 (d, J = 6.91 Hz, 2H), 8.67 (d, J = 6.91 Hz, 2H), 8.34 (d, J = 6.91 Hz, 2H), 8.23 (d, J = 6.59 Hz, 2H), 7.94 (s, 1H), 7.79 (s, 1H), 7.23 (s, 1H), 6.22 (br. s., 2H), 5.07 (t, J = 5.70 Hz, 2H), 4.80 (t, J = 5.00 Hz, 2H), 4.67 (t, J = 7.06 Hz, 2H), 3.79 (t, J = 6.12 Hz, 2H), 2.40 (quin, J = 1.00 Hz, 2H), 1.85 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN, 30 °C): δ = 165.78(s), 157.43(s), 154.05(d), 152.90(s), 151.96(s), 151.70(s),